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Mechanism for converting Al_2O_3-containing borate glass to hydroxyapatite in aqueous phosphate solution

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Abstract

The effect of replacing varying amounts (0–2.5 mol.%) of B_2O_3 with Al_2O_3 in a borate glass on (1) the conversion of the glass to HA in an aqueous phosphate solution and (2) the compressive strength of the as-formed HA product was investigated. Samples of each glass ($10 \times 10 \times 8$ mm) were placed in 0.25 M K_2HPO_4 solution at 60 °C, and the conversion kinetics to HA were determined from the weight loss of the glass and the pH of the solution. The structure and composition of the solid reaction products were characterized using X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. While the conversion rate of the glass to HA decreased considerably with increasing Al_2O_3 content, the microstructure of the HA product became denser and the compressive strength of the HA product increased. The addition of SiO_2 to the Al_2O_3-containing borate glass reversed the deterioration of the conversion rate, and produced a further improvement in the strength of the HA product. The compressive strength of the HA formed from the borate glass with 2.5 mol.% Al_2O_3 and 5 mol.% SiO_2 was 11.1 ± 0.2 MPa, which is equal to the highest strengths reported for trabecular bone. The results indicated that simultaneous additions of Al_2O_3 and SiO_2 could be used to control the bioactivity of the borate glass and to enhance the mechanical strength of the HA product. Furthermore, the HA product formed from the glass containing both SiO_2 and Al_2O_3 could be applied to bone repair.

Keywords: Borate glass; Hydroxyapatite; Bioactivity; Porous structure; Mechanical strength

1. Introduction

Certain glasses, referred to as bioactive glasses, react chemically with aqueous phosphate solutions, such as the body fluids in humans and animals, forming a hydroxyapatite (HA) layer that bonds strongly to hard or soft tissues [1,2]. Both silicate-based and borate-based glasses, as well as glass ceramics, have been observed to be bioactive [3–6]. There is a growing interest in the use of these bioactive glasses and glass ceramics in biomedical applications, such as bone repair, fixation of long-bone fractures and periodontal repair [4–6].

A key property of bioactive glasses is their ability to convert to HA, sometimes referred to as their bioactive potential. While there is no standard test, the bioactive potentials of different glasses are often compared in vitro by measuring the rate at which they covert to HA when placed in an aqueous phosphate solution under a controlled set of conditions (concentration of phosphate ions, concentration of glass in the solution, starting pH of the solution and temperature). The bioactive potential

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in vitro has been shown to correlate with the bioactivity in vivo [7].

The effect of compositional modification on the bioactive potential of silicate-based bioactive glasses was studied by Huang et al. [8,9] for 45S5 bioactive glass and by Yao et al. [10–12] for 13–93 bioactive glass. They replaced varying molar concentrations of SiO_2 in the baseline glasses with B_2O_3, and studied the rate at which glass particles (typically of size 150–300 μm) converted to HA. Because of their lower durability, the borate equivalents of these silicate-based bioactive glasses, in which all the SiO_2 was replaced with B_2O_3, converted considerably faster to HA. For example, the borate equivalent of 45S55 bioactive glass, designated 45S5–3B, converted almost completely to HA within 3–4 days, whereas only ~50% of 45S5 glass was converted after several weeks.

Although the 45S5–3B glass exhibited excellent bioactivity both in vitro and in vivo [11–13], the degradation rate, as determined by its conversion to HA, may be too fast to match the growth rate of new bone. Furthermore, the HA products formed from borate bioactive glasses have a porous, weak structure, with compressive strengths lower than that reported for human trabecular (or spongy) bone (2–12 MPa). Because of its low mechanical strength, the use of borate-based bioactive glass for repairing defects in load-bearing bones may be limited. Therefore, many other types of borate-based glass with different compositions have been investigated to control the biodegradation and improve the mechanical properties of the HA product [14–18].

Previous work has shown that the addition of Al_2O_3 to silicate-based bioactive glass in the system $CaO–SiO_2$ reduced the bioactivity, and the addition of more than 1.7 mol.% Al_2O_3 resulted in a suppression of the bioactive potential of the glass, by suppressing the formation of a calcium phosphate layer on the glass surface in a simulated body fluid (SBF) [19]. On the other hand, a borosilicate glass with the composition (in mol.%) of: 40.0 B_2O_3, 7.5 SiO_2, 40.0 CaO, 8.0 Na_2O, 2.0 Al_2O_3 and 2.5 P_2O_5 showed significant bioactivity by forming HA on its surface when placed in a dilute phosphate solution, even though the Al_2O_3 content was as high as 2.0 mol.% [14,16]. The early stage of the conversion process for this glass (<5 h) resulted in the formation of brushite ($CaHPO_4{\cdot}2H_2O$), which later converted to HA, indicating that this borosilicate glass with a small amount of B_2O_3 replaced by Al_2O_3 had a different conversion mechanism when compared to borate and borosilicate glasses.

The objective of the present work was to investigate the effect of replacing varying amounts (0–2.5 mol.%) of B_2O_3 with Al_2O_3 in a borate glass on the conversion of the glass to HA in an aqueous phosphate solution and on the compressive strength of the as-formed HA product. The conversion to HA was monitored by measuring the weight loss of the glass and the pH of the phosphate solution. The structure, composition and compressive strength of the conversion products were characterized. The present work is applicable to the development of bioactive glasses with not only controllable conversion rates to HA in a dilute phosphate solution but also compressive strengths within the range reported for human trabecular bone, thereby providing a novel class of scaffold materials for bone tissue engineering.

2. Experimental procedure

2.1. Preparation of glass samples

The parent borate glass used in the present work had a composition (molar concentration) of $2Na_2O{\cdot}2CaO{\cdot}6B_2O_3$, which was designated as NCB glass. The other glasses used in the present work, designated ANCB glasses, had the same molar content of Na_2O and CaO, but with varying molar concentrations of B_2O_3 replaced by Al_2O_3. The compositions of the glasses in weight percent (wt.%) and mole percent (mol.%) are given in Table 1.

The NCB and ANCB glasses were prepared by melting the required quantities of Na_2CO_3, $CaCO_3$, H_3BO_3 and Al_2O_3 (Reagent grade; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) in a platinum crucible for 30 min at 1200 °C in air. The melt was cast into preheated steel molds to form bulk glass samples with a size of $10 \times 10 \times 8$ mm. After casting, the samples were annealed in air for 2 h at 500 °C, and cooled slowly to room temperature.

2.2. Glass conversion in a phosphate solution

The phosphate solution used in the conversion reaction was prepared by dissolving K_2HPO_4 (Reagent grade; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) in deionized water to give a concentration of 0.25 M, and the starting pH value was adjusted to 9.0 ± 0.1 by adding small quantities of dilute HCl solution. Each reaction system consisted of a glass sample ($10 \times 10 \times 8$ mm) in 800 ml of phosphate solution at 60 °C, which corresponded to 1 mm^2 of initial glass surface area in 1 ml of solution. Compared with the human body fluid, the phosphate solution had a higher pH value and higher temperature, as well as higher phosphate ion ($(PO_4)^{3-}$) concentration. The higher temperature was chosen to enhance the conversion rate of the glass in order to compare the bioactivity of the different glasses within a reasonable time scale for the experiments, and the higher phosphate concentration ensured that sufficient $(PO_4)^{3-}$ ions were available in the solution to react with all the Ca^{2+} ions from the glass to precipitate stoichiometric HA ($Ca_{10}(PO_4)_6(OH)_2$).

2.3. Weight loss and pH value measurement

During the conversion reaction, Na^+ and $(BO_3)^{3-}$ ions from the glass dissolved into the solution, whereas the Ca^{2+} from glass reacted with $(PO_4)^{3-}$ to precipitate HA [13], which resulted in a decrease in the mass of the glass

ID	Title	Pages
1528	Mechanism for converting Al2O3-containing borate glass to hydroxyapatite in aqueous phosphate solution	9